

# **Volume 4: Potential Ground and Surface Water Impacts**

## ***Chapter 1: Potential Scenarios for Ethanol- containing Gasoline Released into Surface and Subsurface Waters***

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# **1. Potential Scenarios for Ethanol-containing Gasoline Released into Surface and Subsurface Waters**

## **1.1. Introduction**

If California introduces the use of ethanol as a fuel oxygenate, a variety of scenarios may be anticipated in which either bulk fuel-grade ethanol or gasoline blended with ethanol (gasohol) may be released into the environment during its production, distribution, and use. The purpose of this chapter is to use a life-cycle approach (that is, the production, distribution, and use of ethanol) to review systematically the potential release scenarios that may impact California's surface and subsurface waters. The discussion of these scenarios includes field studies wherever possible to identify potential surface and groundwater impacts associated with a scenario.

Figure 1-1 summarizes the life-cycle phases of production storage, blending, distribution, and use of ethanol and gasohol. Table 1-1 summarizes the various potential release scenarios. The table includes a brief description of each release site assumptions and risk assessment issues that may be important during the consideration of each scenario. Also included in the table are qualitative descriptions of the likelihood of occurrence for the scenario, risk-management options, and other release considerations.

## **1.2. Production**

Currently, ethanol is produced primarily in the Midwest from domestic grain. (California has the potential in the future to produce ethanol from recycled biomass [California Energy Commission, 1999]). Most large ethanol producers use a process called "wet-milling" to separate the starch from the grain prior to fermentation of the starch. The highly purified starch is used as the feedstock for ethanol (American Coalition for Ethanol [ACE], 1999). Small processors, however, still use whole-grain fermentation processing which does not first separate out starch through wet-milling and leaves more impurities in the final ethanol product which are not removed.

During the production of ethanol, bulk fuel-grade ethanol (that is, fuel ethanol) is typically stored in large-capacity, above-ground storage tanks (ASTs). Bulk fuel ethanol releases from ASTs and associated piping may also contain other compounds that are byproducts of the fermentation and the subsequent distillation process, or that have been added as amendments.

### **1.2.1. Trace Compounds Introduced during the Production of Fuel-grade Ethanol**

#### **1.2.1.1. Process Impurities**

When purified starch is used to produce ethanol, the recovered bulk fuel ethanol is relatively free of production byproducts except for glycerol and fusel oil. Glycerol is a major byproduct

(about 5–10% of the quantity of ethanol) of fermentation (Karaosmanoglu *et al.*, 1996); however, glycerol has a boiling point higher than 200°C and is an unlikely contaminant in the final distilled ethanol product.

Another byproduct of the industrial fermentation process is “fusel oil,” an alcohol mixture with a boiling range of 80–132°C. The amount and the composition of fusel oil produced in the fermentation process depend on the raw materials used. A typical fusel-oil production ratio during the fermentation process is 0.2–0.7% (wt) on the basis of pure ethanol (Karaosmanoglu *et al.*, 1996). Although 50 different compounds have been identified in fusel oil, its major components are fermentation amyl alcohols, such as 2-methyl-1-butanol and 3-methyl-1-butanol (Karaosmanoglu *et al.*, 1996).

There are also other compounds, such as acetaldehydes and ethyl acetate, present as process impurities. However, the concentration of these byproducts in fuel ethanol is only in the milligrams-per-liter (mg/L) range when purified starch is used as the feedstock.

Fuel ethanol produced from whole grain contains substantially more impurities (Karaosmanoglu *et al.*, 1996). These byproducts are derived from the non-starch portions of the whole grains, such as hemicellulose and pectin, which contain methyl and acetyl groups. Upon hydrolysis, methanol and acetic acid are formed. These byproducts are subsequently distilled together with ethanol. Whole-grain processing also produces a higher quantity of fusel oil in fuel ethanol. These byproducts are not separated out of fuel ethanol by distillation and so are delivered with the final product.

Methanol is another common process impurity in fuel ethanol. Typically, fuel ethanol consists of the following: 95.1 wt% ethanol, 4.8 wt% water, and 0.1 wt% higher alcohols (Paul, 1978). At the time of blending, fuel alcohol must meet the criteria in Table 1-2.

### 1.2.2. Additives

Denaturants—toxic or noxious materials used to make the ethanol unfit for human oral consumption—must be added to fuel ethanol directed to storage. Commonly used denaturants for fuel ethanol are unleaded gasoline or rubber hydrocarbon solvent. These are added to ethanol at a minimum of 2% by volume, as defined by formula CDA 20 of the Bureau of Alcohol Tobacco and Firearms of the U.S. Treasury Department (American Society of Testing and Materials [ASTM], 1995). This specification prohibits the use of hydrocarbons, such as kerosene, with a boiling point higher than 225°C. Thus, only hydrocarbons in the gasoline boiling range can be used as denaturants (ASTM, 1995).

Denatured fuel ethanol may contain other additives, such as corrosion inhibitors and detergents (ASTM, 1995). Various blending agents also have been used in fuel alcohol-gasoline mixtures to lower the phase-separation temperature of the blends to below ambient temperatures experienced during the winter season (Karaosmanoglu *et al.*, 1996). These blending agents can be grouped as aromatic compounds, higher aliphatic alcohols, and aromatic alcohols. The addition of other materials is prohibited.

In the final product, the ethanol component of denatured fuel ethanol, excluding water, must comprise at least 98% by volume and must not contain more than 0.5% by volume of methanol or total ketones, or both. Furthermore, the total ethanol content of denatured fuel ethanol, including impurities, must be no less than 95% by volume (ASTM, 1995). A summary of the

trace compounds created or introduced during production and processing of fuel ethanol is shown in Table 1-3. This table shows no additional trace elements that are noteworthy of concern due to their solubility and associated toxicity compared to other common gasoline components. None of these trace compounds is substantially less biodegradable than other common gasoline components.

### **1.3. Distribution**

#### **1.3.1. Distribution of Bulk Fuel Ethanol**

Shipments of ethanol to California could average about 46 million gal per month and could be as high as 50 million gal per month during the summer peak driving season. A combination of rail transport and marine cargo is likely to be used to distribute bulk ethanol to the California market. Initially, approximately 80% of the bulk ethanol destined for California will be shipped in railroad tanker cars that typically contain about 29,000 gal. Approximately 1600 rail car movements per month would be needed to meet demand (Downstream Alternatives, Inc., 1999). Strings of railroad tankers may be piped together to form a unit train “rolling pipeline.” This arrangement allows a string of tanker cars to be emptied quickly, permitting transport turnaround times of about two weeks between production facilities in the Midwest and distribution terminals in California (Jaffoni, 1999).

Initially, about 20% of the bulk ethanol will be transported as marine cargo. In this scenario, 10,000-barrel tanker barges would float the bulk fuel ethanol down the Mississippi River to New Orleans where it would then be transferred to large-capacity marine tankers for transport to Pacific coast terminals. Marine tanker cargoes most likely would be about 4–5 million gal but may be as large as 10–12 million gal (Downstream Alternatives, Inc., 1999; Jaffoni, 1999).

According to a California Energy Commission analysis (Schremp, 1999), two distribution hubs—one in Northern California and one in Southern California—would receive the bulk fuel ethanol. The volume of bulk fuel ethanol entering California as marine cargo is expected to increase over time to as much as 80% because distribution terminals prefer receiving single shipments of large quantities to minimize the labor- and time-intensive handling of rail cars (Jaffoni, 1999).

Presently, refiners and pipeline operators are reluctant to distribute bulk fuel ethanol through a pipeline because of concerns regarding ethanol’s affinity to water. Water is often present in association with unblended gasoline transported through the pipelines (Center for Transportation Research, no date). If this issue can be addressed, more pipeline use can be anticipated.

#### **1.3.2. Blending of Ethanol with Gasoline**

Because of the limitations in pipeline use, about 77% of the bulk fuel ethanol would be distributed by tanker trucks from the distribution hubs to blending terminals. It is expected that truck traffic would increase in proximity to the distribution hubs (Schremp, 1999). Pipelines will continue to be used to deliver a base gasoline to blending terminals for blending with fuel ethanol. The bulk fuel ethanol and base blending gasoline will be stored in separate tanks and blended just prior to shipment to gas stations. Several blending processes are available (Downstream Alternatives, Inc., 1999):

- **Tank Blending:** This alternative requires a recirculation capacity within the storage tank. This is the least preferred method because of the possibility of water contamination of the blended fuel which may lead to separation during distribution.
- **Top-off/Splash Blending:** In this blending process, ethanol and base gasoline are delivered separately into a tanker truck. The mixing during loading and transport accomplish the blending process. This process is widely and successfully used and is the preferred method for developing distribution systems.
- **In-line/Injection Blending:** Ethanol and gasoline are blended in-stream as the mixed fuel is delivered to a tanker truck. This is the preferred method of blending for established distribution systems because of better quality control and fewer blending errors.

### 1.3.3. Transportation and Storage of Blended Gasohol

Tanker trucks will transport the gasohol (that is, gasoline blended with ethanol) much as it is currently done. The typical gas station operates at least two underground storage tanks of between 10,000 and 20,000 gal each. High-throughput gas stations may receive a tanker-truck delivery at least once a day. If only two tanks are operated, mid-octane gas is often dispensed by blending a lower- and a higher-octane gasoline at the pump.

Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and the three isomers of xylene (BTEX) are ubiquitous groundwater pollutants commonly associated with petroleum product releases from underground storage tanks (USTs). All six BTEX compounds are powerful depressants to the central nervous system, and chronic benzene exposure can cause leukemia (*Federal Register*, 1985). Thus, BTEX contamination of potential drinking water sources represents a serious threat to public health. To put the magnitude of this problem in perspective, 370,000 fuel releases from leaking underground storage tanks (LUST) have been confirmed in the United States (U.S. Environmental Protection Agency [U.S. EPA], 1998). The actual number of tank releases could be as high as 600,000 (Flatham, *et al.*, 1994).

In December 1998 federal regulations were placed into effect requiring improved, leak resistant underground gasoline storage tanks (Herman and Fields, 1998). California gas stations are required to have USTs and piping that are double-walled with leak-detection systems capable of detecting line leaks of 3 gal per hour and tank leaks of 3 gal per day (*California Code of Regulations*, Title 23, sections 2610–2728).

Use of a 10% by volume (or less) ethanol blend requires no vehicle engine or fuel tank modification (Canadian Renewable Fuels Association [CRFA], 1999). Currently, retail gasoline dispensing equipment is designed to handle 10% by volume ethanol gasolines although attention should be given to the use of alcohol-resistant materials in the pumps, line leak detectors, hoses, seals, and nozzles (Center for Transportation, no date). Gas stations that convert to dispensing gasohol will need to replace or recalibrate meters, conduct storage tank cleaning and drying, and check storage tank and piping capability for use with ethanol fuels.



## **1.4. Use**

### **1.4.1. Present Extent of Gasohol Use**

Gasohol has been used extensively in the corn-growing states of the Midwest for several years. It can be found as an option at most gasoline stations in Iowa and Nebraska. At present, 60% of gasoline sold in Illinois and 90% of the gasoline sold in the Chicago area contains 10% by volume ethanol (Renewable Fuels Association [RFA], 1999). Between the Chicago and Milwaukee areas, approximately 450 million gal of ethanol are consumed in gasoline annually (Hord, 1999). Gasohol has also been sold in Kansas through independent stations although its availability has declined in the last couple of years because major distributors have bought many of the independent stations (Winn, 1999). Throughout the United States, consumers use more than 15 billion gal of ethanol-blended gasoline each year (ACE, 1999).

In July 1998, there were approximately 950 retailers of ethanol-blended fuels across Canada, excluding those who were not listed with the CRFA (1999). The ethanol-gasolines were distributed by most major petroleum companies (for example, Mohawk Oil; Sunoco, Inc., and MacEwen Petroleum, Inc.) and several other independent retail outlets (Mr. Gas, Pioneer Petroleum, Frances Fuels, Stinson Petroleum, and Sunys). This gasohol was available in all grades of gasoline, and also for on-farm delivery.

During the use of gasohols in vehicles and watercraft, two types of emissions are released: exhaust and evaporative. Exhaust emissions are those exiting the tailpipe during the combustion of gasohols. Evaporative emissions occur while the vehicle is sitting as well as operating. Heat from the engine or from ambient weather conditions can cause volatile components of the fuel, including ethanol, to boil off and leak into the air. The California Air Resources Board has developed emission profiles for proposed 5.8% and 10.1% ethanol blends of motor vehicle fuel (Allen *et al.*, 1999). These emission profiles have been used during our evaluation of potential releases to groundwater from the rainout of these emissions.

Releases of ethanol and blended gasohol during production and distribution are typically point source releases (that is, the extent of the release is a localized area). The environmental concentrations of ethanol or gasoline components associated with point source releases often are, initially, relatively high. On the other hand, the area extent of releases during the use of gasohol is typically quite large, for example, an entire lake, watershed, or air basin. These types of releases associated with the use of gasohol are referred to as non-point source releases, and the environmental concentrations of ethanol and gasoline components associated with these types of release typically are relatively low.

### **1.4.2. Releases from Watercraft Exhaust Emission into Surface Waters**

One of the unexpected surface-water impacts resulting from the use of MTBE in gasoline was MTBE entering surface water in reservoirs and lakes in California (see Malcolm-Pirnie, Inc., 1998; McCord and Schladow, 1998). The principal source of this contamination is recreational boating, with the largest source attributed to two-stroke carbureted marine engines used in jet skis (Allen *et al.*, 1998). Recreational watercrafts typically discharge exhaust below the water

surface. Often this discharge is through the watercraft propeller or propulsion jet, which promotes a thorough mixing of the discharged compounds with surface waters.

Effective June 1, 1999, the Tahoe Regional Planning Agency imposed a ban on certain two-stroke marine engine technologies. Previous studies had shown that while two-stroke carbureted engines accounted for only 11–12% of the total fuel used by watercraft on Lake Tahoe, they were responsible for approximately 90% of the MTBE emissions to the lake (Allen *et al*, 1998). While recent data strongly suggests that the ban on certain types of two-stroke engines at Lake Tahoe was very successful in reducing both MTBE and BTEX (Allen and Reuter, 1999: Appendix C of Chapter 5 of this report), exhaust releases of gasoline containing ethanol can be expected to continue.

### **1.4.3. Releases from Washout of Automotive Tailpipe Emissions and Combustion Products to Surface Waters**

Tailpipe and combustion products generally enter the atmosphere in the vapor phase. In the case of ethanol and methyl tertiary butyl ether (MTBE), these vapors preferentially partition into water present in the atmosphere. During precipitation events, such as rain storms or the formation of dew, the ethanol or MTBE is washed out of the atmosphere and deposited onto the ground surface or surface bodies of water and eventually infiltrates into groundwater. Although the concentrations washed out often are relatively low, the depositions occur over a large area and will continue to be deposited as long as the fuel is used. For these reasons, it is important to consider any cumulative impacts that may result from the ongoing deposition of tailpipe emissions and combustion products.

## **1.5. Field Studies**

### **1.5.1. Bulk Fuel Ethanol Releases with Fuel Hydrocarbons Absent**

Releases of liquid bulk ethanol to soil and water can result from leaks or spills from ASTs at the production site. Few studies have documented the release of bulk ethanol to soils where fuel hydrocarbons are absent. Concentrations of ethanol as high as 2600 parts per million (ppm) were detected at the site of a 30,000-gal spill of denatured alcohol (Chambers, 1999).

Although we found few field studies that deal with bulk releases at ethanol production sites, there was a study of Savasol, a solvent comprised almost entirely of ethanol, that leaked from an UST at an industrial facility in Salem, Massachusetts, in the early 1990s (Schaffner, 1999). The volume of ethanol leaked was unknown. Although initial concentrations were high, ethanol concentrations were non-detectable within six to eight months after the spill event. The groundwater table was near the ground surface in the vicinity of the spill site. It is likely that volatilization in combination with rapid biodegradation were important mechanisms in the rapid natural attenuation of the bulk ethanol at this site.

### **1.5.2. Bulk Fuel Ethanol Releases with Fuel Hydrocarbons Present**

A 1994 American Petroleum Institute (API) survey found that 85% of the monitored AST farms reported groundwater contamination. In view of this fact, bulk ethanol releases at distribution and blending terminals could reasonably be expected to impact already existing fuel hydrocarbon releases. Indeed, as described below, there have been such incidents in states that use gasohol.

Our review of field studies found a few instances in which ethanol was released at sites where fuel hydrocarbons were known to be present. One such study concerned bulk ethanol that was released in the early 1980s from a gasoline distribution terminal owned by Zephyr, Inc., in Leelanau County, Michigan (Skipper, 1999). It is believed that the spill occurred when either a valve or pipe failed during a transfer at the blending rack. The less-than-500-gal spill of ethanol was onto soil which already had a high degree of prior contamination by other petroleum hydrocarbons. Although the distribution of sampling wells at this site was sparse, groundwater samples were analyzed for a very comprehensive suite of petroleum hydrocarbons. Technical reports written about this site did not note any increase in the concentration of petroleum hydrocarbons following the ethanol spill. The ethanol- and petroleum-contaminated soil has since been excavated and landfilled, preventing any long-term analysis of the fate of these contaminants.

An estimated 17,740 gal of denatured ethanol was released in September 1992 from an AST at a bulk storage terminal in Tacoma, Washington (Hooton, 1999). The leak was attributed to a faulty water draw valve. The area surrounding the spill site had previously been contaminated by a variety of petroleum products. Free-product and groundwater recovery, and soil vapor extraction remediation measures were ongoing at the site before the ethanol spill.

Groundwater and soil sampling efforts at the Tacoma, Washington, site were not initially implemented due to the lack of regulatory concern by the Washington state Department of Ecology (O'Hara, 1993). In August 1994—almost two years after the initial spill event—groundwater samples were collected and analyzed for ethanol. Concentrations of ethanol in the immediate vicinity of the tank that leaked ranged from 5,600 to 81,000 ppm (about 8% ethanol by mass) (EMCON, 1997). However, no ethanol was detected in these same wells in May 1997, approximately five years after the spill.

While data in this case are insufficient to thoroughly assess the overall impact of ethanol on the existing light nonaqueous phase liquid (LNAPL) contamination, or benzene, toluene, ethyl benzene, and xylene (BTEX) concentrations, evidence suggests that benzene concentrations increased in the immediate vicinity of the tank as a result of high ethanol concentrations. Data quantifying benzene concentrations before and after the ethanol spill are only available for one well. Benzene concentrations two to five years after the spill (10–20 mg/L) were more than an order of magnitude higher than that three years before the spill (0.88 mg/L) (Dalton, 1998). Although the lack of data prevents a thorough analysis of the effects of ethanol, it can be concluded that the area within 20 ft of the ethanol spill generally has significantly higher benzene concentrations than at other areas at the bulk petroleum distribution terminal.

The impact of the ethanol spill on the distribution of light non-aqueous phase petroleum hydrocarbons (free product) at the Tacoma, Washington, site is unclear. Professionals who have

studied this site conflict in their assessment of the amount of free product at the site before the ethanol spill (Dalton, 1998; EMCON, 1997). Because of these conflicting interpretations of the initial conditions, changes in the nature of the free product cannot be quantified.

In March 1999, an unknown amount of ethanol was released from an AST at a bulk fuel ethanol terminal in the Pacific Northwest where petroleum hydrocarbons were also present. The volume of the bulk fuel ethanol released is estimated to be greater than 10,000 gal (Buscheck, 1999). Groundwater sampling data from this site is much more extensive than that available at other sites. At least ten additional wells were installed to monitor the fate of ethanol and BTEX at this site; however, analysis of the database of groundwater concentrations has not yet been completed. Groundwater was sampled in June and August 1999, with additional rounds of sampling possible in the near future. Shortly after the spill event, concentrations of ethanol in the groundwater ranged from 0.2 to 20,000 mg/L. Preliminary interpretation suggests that by the August 1999 sampling period, less than five months after the spill itself, ethanol concentrations in the groundwater were below detection limits.

Significant petroleum contamination existed at this site prior to the ethanol spill. BTEX and total petroleum hydrocarbons (TPH) had been detected in soil samples although no free product had been observed in the immediate vicinity of the ethanol tank. Preliminary analysis of the groundwater concentration data suggests that BTEX concentrations are on the order of a factor of two greater than before the ethanol spill.

### **1.5.3. Releases of Gasohol from Tanker Truck**

Recent spills of gasohol from tanker trucks are treated as emergency response actions and generally the site of these spills receive no long-term environmental monitoring. Therefore, there is little data about residual impacts from such releases.

### **1.5.4. Gasohol Releases from Gas Station Underground Storage Tanks**

With the current widespread use of gasohol, it is expected that there would be numerous releases of gasohol from LUSTs. As part of the review conducted for this chapter, information was gathered on the extent and knowledge base available about such sites. The data collection methods included telephone interviews with state and US EPA personnel in Midwestern states who investigate and remediate LUSTs, contact with Bruce Bauman of the API, and a general request for information through an electronic mailing list to groundwater professionals.

From these contacts, it appears that there is inadequate information available to identify and investigate the impact of ethanol on the fate of BTEX species from LUST sites at gasoline stations. Although the persons who were interviewed acknowledged that there must be gasohol spill sites in each of the Midwestern states, there is no knowledge base associated with potential differences in the nature or extent of groundwater contaminated by gasohol versus gasolines not containing ethanol.

David Chambers of the Nebraska Department of Environmental Quality (NDEQ) searched the NDEQ database for spill sites related to "gasohol," "alcohol," or "ethanol" (Chambers, 1999). Of the 39 entries found, 11 were associated with gasohol or ethanol-diesel mixtures (see

Appendix A for database search results). For the one railroad accident involving a 114,000-gal alcohol diesel release, no ethanol was detected in the groundwater.

### 1.5.5. Summary of Knowledge Gained from Field Studies

In general, the information presently available on the fate of BTEX and ethanol at field sites confirms the expected behavior based on the literature reviews presented in Chapters 2 and 3 of this volume. Although the information is sparse, it appears that when neat ethanol is spilled, the ethanol concentrations drop quickly in the subsurface via natural attenuation mechanisms. There is, however, a risk of elevated BTEX concentrations in groundwater following the release of bulk ethanol into soil previously contaminated with petroleum products. A significant opportunity exists to learn more from the ethanol spill site in the Pacific Northwest. Substantial data was collected in a timely fashion at that site and further analysis could prove extremely valuable. An effort to rigorously interpret this data could lead to substantial improvements in our understanding of the fate of ethanol and BTEX in the subsurface.

For gasohol spills or LUFT releases at gasoline stations, much of the lack of information stems from the regulatory environment controlling the investigation and remediation of gasoline leaks and spills. None of the states requires that ethanol concentrations be measured in groundwater samples because ethanol is not a regulated pollutant. Similarly, databases used for tracking release sites do not include a mechanism to identify or sort releases of gasohol versus non-ethanol gasolines. This is due in part to the perception that there are no important qualitative differences in environmental impact between the two types of gasoline. Further, there is no means of ascertaining the type of gasoline released at many sites. Perhaps, as was the case with MTBE less than a decade ago, regulators and groundwater professionals are not yet looking for any impacts because they do not perceive nor systematically evaluated gasohol as having an important effect on impacts due to groundwater contamination.

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## ***Figures***



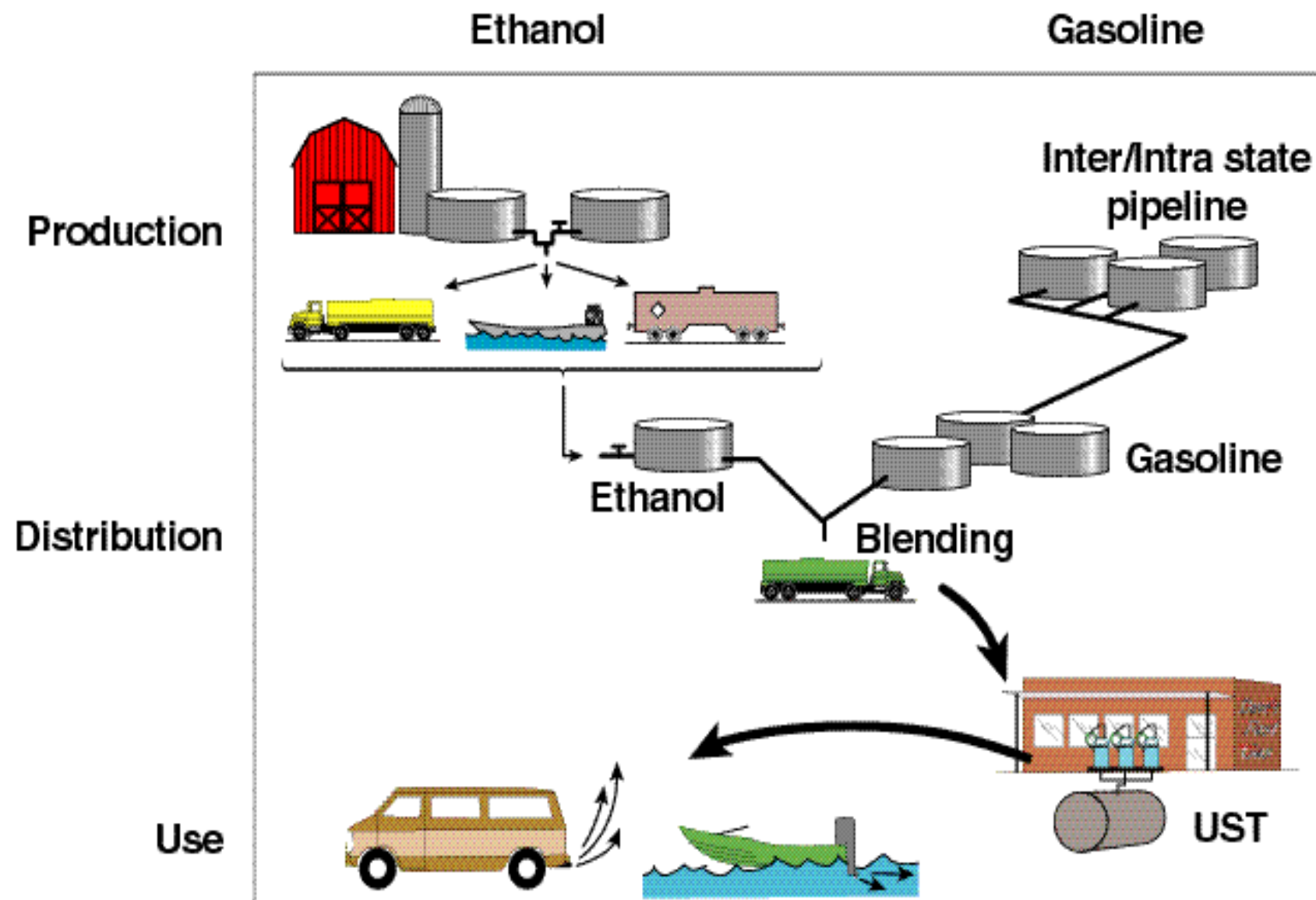


Figure 1-1. Life-cycle of fuel ethanol.



## ***Tables***



**Table 1-1. Life-cycle assessment of ethanol releases.**

<b>Release scenario</b>	<b>Release assumptions</b>	<b>Site assumptions</b>	<b>Likelihood of occurrence</b>	<b>Risk assessment issues</b>	<b>Risk management options</b>
<b>Production</b>					
<i>Release from an aboveground storage tank (AST) at production site</i>	<i>Assumes a large-volume (&gt;30,000 gal) bulk ethanol release to soils and groundwater from a high-volume AST or associated piping at an ethanol-manufacturing site.</i>	<i>Assumes bulk ethanol release into relatively pristine subsurface conditions. Fuel hydrocarbons are assumed to be historically absent.</i>	<i>Small likelihood of occurrence.  Because California currently has few ethanol production facilities, this scenario represents a release that could occur only once biomass ethanol production facilities are constructed in the state in the future.</i>	<i>Toxicity to ecological receptors in direct contact with the release. Case studies indicate that ethanol is relatively rapidly lost in the subsurface environment.</i>	<i>Engineered containment to control potential release, e.g., double-walled tanks and piping. Spill prevention and containment contingency (SPCC) Plans typically in place.</i>
<b>Distribution</b>					
<i>Release during bulk ethanol transport by rail or highway</i>	<i>Assumes that a rupture of a rail tank car or a tanker truck releases a large volume of bulk ethanol (10,000–30,000 gal) to soils and groundwaters or surface waters.</i>	<i>Assumes a relatively pristine surface and subsurface conditions where fuel hydrocarbons are historically absent.</i>	<i>Moderate likelihood of occurrence. Because California currently has few ethanol production facilities, most ethanol used will initially be imported into the state by way of rail tank car or tanker truck.</i>	<i>Toxicity to ecological receptors in direct contact with the release. Potential to impact surface aquatic ecosystem. It is likely that volatilization as well as biodegradation will be important mechanisms in the rapid natural attenuation of the bulk ethanol.</i>	<i>Rail car and truck tanker releases are typically treated as an emergency response action and generally require no long-term monitoring.</i>

**Table 1-1. Life-cycle assessment of ethanol releases (Cont.).**

Release scenario	Release assumptions	Site assumptions	Likelihood of occurrence	Risk assessment issues	Risk management options
<b>Distribution (Cont.)</b>					
<i>Release during bulk ethanol transport by marine cargo tanker</i>	<i>Assumes that a rupture of a marine tanker ship releases a large volume of bulk ethanol (&gt;100,000 gal) into marine surface waters. While ethanol is infinitely soluble, it will tend to distribute near the water surface because it is less dense than water.</i>	<i>Assumes a bulk ethanol release into the near-shore coastal marine environment.</i>	<i>Low likelihood of occurrence.  However, the shipment of ethanol as marine cargo will increase because distribution hubs will prefer to receive larger quantities to minimize the handling of rail cars.</i>	<i>Toxicity to ecological receptors in direct contact with the release; potential to impact surface aquatic ecosystem. It is likely that volatilization, dispersion, and dilution as well as biodegradation will be important mechanisms in the rapid natural attenuation of the bulk ethanol.</i>	<i>Requires bulk ethanol to be shipped in marine tankers with double-walled construction.</i>
<i>Release of bulk ethanol at a distribution terminal</i>	<i>Assumes a large volume bulk ethanol release to soils and groundwater at a distribution hub or terminal. The release is assumed to be from a high volume AST or associated piping. ASTs at a distribution hub may contain &gt;150,000 barrels of ethanol.</i>	<i>Fuel hydrocarbons are assumed to be historically present and may be present as free product trapped in the subsurface. MTBE may be present in the free product.</i>	<i>Moderate likelihood of occurrence.</i>	<i>The ethanol is assumed to interact with soils contaminated with existing fuel hydrocarbons. Previously immobile hydrocarbons may now be mobilized to the groundwater. An existing fuel hydrocarbon groundwater plume may be expanded.</i>	<i>Engineered containment to control release, e.g. double-walled tanks and piping. SPCC Plans typically in place. Manage the location of ethanol ASTs to avoid known areas of fuel hydrocarbon releases. Remediate the fuel hydrocarbon releases.</i>



**Table 1-1. Life-cycle assessment of ethanol releases (Cont.).**

<b>Release scenario</b>	<b>Release assumptions</b>	<b>Site assumptions</b>	<b>Likelihood of occurrence</b>	<b>Risk assessment issues</b>	<b>Risk management options</b>
<b>Distribution (Cont.)</b>					
<i>Release of blended gasohol during transport from a California distribution terminal</i>	<i>Assumes that ethanol is blended with gasoline at a distribution terminal or refinery and transported by tanker truck to a gas station. Assumes a large volume (~5000 gal) of blended gasoline/ ethanol (10% or 6% gasohol) released from tanker truck to soils and groundwaters or surface waters.</i>	<i>Assumes release occurs into roadside environments where fuel hydrocarbons are historically absent.</i>	<i>Moderate likelihood of occurrence.</i>	<i>If any gasohol infiltrates into the subsurface, it will act as a source of groundwater contamination. Concentrations of BTEX in groundwater may initially be somewhat higher than for standard gasoline spill. Potential for a release to streets and urban storm drains.</i>	<i>Tanker cars and truck releases are typically treated as an emergency response action and generally require no long-term monitoring</i>
<i>Release at gas station during underground storage tank (UST) filling</i>	<i>Assumes that gasohol is spilled during UST filling at a gas station. A low-volume (&lt; 50 gal) of blended gasoline/ ethanol (10% or 6% gasohol) released to soils and groundwater.</i>	<i>Assumes small masses of fuel hydrocarbons are historically present in the subsurface.</i>	<i>A likely and common release scenario.</i>	<i>The ethanol is assumed to interact with soils contaminated with existing fuel hydrocarbons. MTBE may be present.</i>	<i>UST over-fill buckets associated with upgraded USTs should minimize these releases.</i>

**Table 1-1. Life-cycle assessment of ethanol releases (Cont.).**

<b>Release scenario</b>	<b>Release assumptions</b>	<b>Site assumptions</b>	<b>Likelihood of occurrence</b>	<b>Risk assessment issues</b>	<b>Risk management options</b>
<b>Distribution (Cont.)</b>					
<i>Release at a gas station from a small UST puncture</i>	<i>Assumes a small puncture of the UST or associated piping resulting in a low-volume release of blended gasohol (~&lt;3 gal per day).</i>	<i>Assumes release may occur into sub-surface environments with or without historic fuel hydrocarbon contamination. MTBE may be present.</i>	<i>A likely and common release scenario. Evaluation of this scenario will be important to estimating potential impacts to groundwater resources.</i>	<i>This scenario has the potential to release a large cumulative mass of gasohol because of the large number of USTs in operation and the potential for small leaks to go undetected.</i>	<i>Current requirement for USTs to use double-walled containment reduce the likelihood of this scenario's occurrence. There remain some issues with materials compatibility with ethanol.</i>
<i>Release at a gas station from large UST puncture</i>	<i>Assumes a large puncture of the UST or associated piping resulting in a high-volume release of blended gasohol (~&lt;10 gal per day).</i>	<i>Assumes releases may occur into subsurface environments with or without historic fuel hydrocarbon contamination. MTBE may be present.</i>	<i>Moderate likelihood of occurrence.</i>	<i>Typically, larger UST leaks are rapidly detected, and corrective action is initiated.</i>	<i>Current requirement for USTs to use double-walled containment reduce the likelihood of occurrence. Some issues with materials compatibility with ethanol remain.</i>

**Table 1-1. Life-cycle assessment of ethanol releases (Cont.).**

<b>Release scenario</b>	<b>Release assumptions</b>	<b>Site assumptions</b>	<b>Likelihood of occurrence</b>	<b>Risk assessment issues</b>	<b>Risk management options</b>
<b>Use</b>					
<i>Release from watercraft emissions into surface waters.</i>	<i>Assumes a significant percentage of fuel released through exhaust as uncombusted free product.</i>	<i>Assumes pristine freshwater lakes and rivers.</i>	<i>A likely and common release scenario</i>	<i>The biodegradation and volatilization of ethanol in surface waters is expected to be rapid. Low increases in nutrient loading and decreases in dissolved oxygen concentrations may occur.</i>	<i>Increase engine combustion efficiency.</i>
<i>Release due to rainout of tailpipe emissions and combustion products to surface soils and waters.</i>	<i>Assumes ethanol vapors and combustion products will partition into atmospheric moisture.</i>	<i>Assumes widespread nonpoint source deposition with various amounts of recharge to groundwaters and runoff to surface waters.</i>	<i>A likely and common release scenario.</i>	<i>Ethanol emissions preferentially partitions into water and will be expected to rainout. The biodegradation of ethanol in surface waters is expected to be rapid.</i>	

**Table 1-2. Summary of fuel-grade alcohol at time of blending as specified by ASTM Specification D4806-95.<sup>a</sup>**

Description of trace compound	Maximum content
<i>Water content, max, mass %</i>	1.25
<i>Existent gum, max, mg/ 100 mL</i>	5
<i>Chloride ion content, max, mass ppm</i>	40
<i>Copper content, max, mg/ kg</i>	0.1
<i>Acidity (as acetic acid), max, mass %</i>	0.007
<i>Appearance</i>	<i>Visibly free of suspended or precipitated contaminants (clear and bright)</i>

<sup>a</sup> Source: American Society of Testing and Materials (ASTM), 1995.

**Table 1-3. Trace compounds introduced during production of fuel-grade ethanol.<sup>a</sup>**

Impurities	Denaturants	Blending agents	Additives
<i>Methanol</i>	<i>Unleaded gasoline</i>	<i>Aromatic compounds</i>	<i>Corrosion inhibitors</i>
<i>Fusel oil: amyl and isoamyl alcohols</i>	<i>Rubber hydrocarbon solvent; hydrocarbons with end boiling point &lt;225°C (437°F)</i>	<i>Aromatic alcohols Higher alcohols</i>	<i>Detergents</i>

<sup>a</sup> The total content of impurities, denaturants, blending agents, water, and additives must be less than 5% (by volume) of fuel alcohol (ASTM, 1995).

**Appendix A**  
***Results of Search of NDEQ Spill Database***



# Appendix A

## Results of Search of NDEQ Spill Database<sup>1</sup>

### Nebraska Department of Environmental Quality LUST/ER Section (402)471-4230 Ethanol Release Incidents

SPILL NUMBER	MATERIAL	QUANTITY	UNITS	PRJ MGR	STATUS	INCIDENT TYPE
* 070693-QK-1100	GASOL & DIESEL		UNK	KRIKAC	SUSPENDED	LUST
122698-JB-0725	DENATURED ALCOHOL	30000.00	GAL	SURFACE SPILL		FIXED FACILITY
083195-JF-1400	METHANOL		UNK	SURFACE SPILL	NFA	RAILROAD
091194-JF-1315	RESIDUE DENATURED ALCOHOL		UNK	SURFACE SPILL	NFA	FIXED FACILITY
030292-DT-0845	MOMETHANOLAMINE		UNK	SAR GROUP	NFA	LUST
012198-JF-0001	ISOPROPANOL ALCOHOL		UNK	SAR GROUP	NFA	FIXED FACILITY
061298-KM-1619	2 BUTOXYETHANOL	1.60	GAL	SURFACE SPILL	NFA	LUST
* 061193-QH-1100	DIESEL AND GASOL		UNK	FOGERTY	NFA	FIXED FACILITY
* 072999-JF-0001	GASOL		UNK	SAR GROUP	NFA	LUST
102894-JF-1015	DENATURED ALCOHOL		UNK	SURFACE SPILL	NFA	LUST
* 042893-NH-0545	ALCOHOL DIESEL	114000.00	UNK	SURFACE SPILL	NFA	RAILROAD
012094-AP-0002	190 PROOF ALCOHOL		UNK	SAR GROUP	NFA	RAILROAD
042399-JF-0010	KEROSENE & DENATURED ALCOHOL		UNK	SAR GROUP	NFA	LUST
111693-JF-0000	SOLVENTS, ETHYL ALCOHOL, BARSO		UNK	SAR GROUP	NFA	LUST
120391-JF-0000	ALCOHOL		UNK	SAR GROUP	NFA	LUST
* 120195-AP-0003	GAS, DIESEL, ALCOHOL		UNK	YANG	NFA	LUST
* 060577-RRV-1100	MASTE SOLV, TOLUENE, ALCOHOL	0.00	UNK	SAR GROUP	NFA	LUST
* 092198-JF-0003	ETHANOL & DIESEL		UNK	SAR GROUP	NFA	LUST
AP5490	METHANOL, GAS DIESEL		UNK	SAR GROUP	NFA	LUST
091793-NH-1450	DENATURED ALCOHOL	2.00	LB	SURFACE SPILL	NFA	RAILROAD
080195-BI-1314	MIX OF ALCOHOL/KETONES	2.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
101592-EL-1403	ETHYL ALCOHOL	3.00	GAL	SURFACE SPILL	NFA	LUST-EXEMPT TANK
101794-KM-1455	26% MONOETHANOLAMINE	300.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
011998-JB-1030	ISOPROPYL ALCOHOL	400.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
122298-KM-1113	ETHANOL	506.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
122198-SM-1910	ETHANOL	3465.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
110795-QK-0900	ETHANOL		GAL	SURFACE SPILL	NFA	FIXED FACILITY
082196-KM-0840	ZINC ALCOHOL MIXTURE	5.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
* 082492-DT-0630	METHANOL ALCOHOL	1.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
* 030611-MBS-1030	GASOL	9.00	GAL	MAN	NFA	AIR RELEASE
031001-DMT-0700	GRAIN ALCOHOL	100.00	GAL	SURFACE SPILL	NFA	LUST
080697-JB-1100	ALCOHOL		GAL	SURFACE SPILL	NFA	MOTOR VEHICLE
052598-KM-1507	FURFURYL ALCOHOL	20000.00	LB	SURFACE SPILL	NFA	RAILROAD
031596-JF-0230	ISOPROPYL ALCOHOL	500.00	LB	SURFACE SPILL	NFA	ABOVEGROUND TANK
061193-JB-1230	ETHYL ALCOHOL	13000.00	LB	SURFACE SPILL	NFA	FIXED FACILITY
* 081992-AP-0003	DIESEL & GASOL		UNK	SAR GROUP	NFA	ABOVEGROUND TANK
* 080592-JB-1029	GASOL		UNK	BACKLOG	BACKLOG	LUST
* AP0740	GASOL		UNK	BACKLOG	BACKLOG	LUST
* AP7005	GASOL		UNK	BACKLOG	BACKLOG	LUST

Database Selection Criteria:

Material like "GASOL"  
Material like "ETHANOL"  
Material like "ETHYL ALCOHOL"  
Material like "ALCOHOL"

<sup>1</sup> Provided by David Chambers, NDEQ (Chambers, 1999).

## **Reference**

Chambers, D. (1999). (Nebraska Department of Environmental Quality). Personal letter to S. E. Powers, September 13.











Table 1-2 & 3